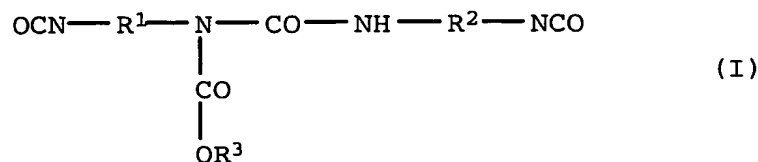


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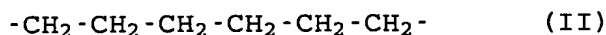
Diisocyanates with allophanate groups derived from alicyclic alcohols

5 The present invention relates to diisocyanates of the formula (I)



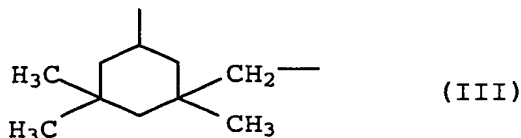
10 in which the radicals have the following meanings:

$\text{R}^1, \text{R}^2$ : both radicals a radical of the formula (II)



(diisocyanates Ia)

20 one radical a radical of the formula (II) and the other radical a radical of the formula (III)



(diisocyanates Ib)

both radicals a radical of the formula (III) (diisocyanates Ic),

30  $\text{R}^3$ : - a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by  $\text{C}_1$ - $\text{C}_4$ -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a  $\text{C}_1$ - $\text{C}_4$ -alkyl radical, or

- a  $\text{C}_1$ - $\text{C}_4$ -alkyl radical in which one hydrogen atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by  $\text{C}_1$ - $\text{C}_4$ -alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a  $\text{C}_1$ - $\text{C}_4$ -alkyl radical; a pyrrolidone radical or a morpholine radical, where in the case of the two last-mentioned radicals the nitrogen atom is attached to the alkyl radical.

The invention additionally relates to isocyanate mixtures and to 2-component coating compositions which comprise these isocyanates; coating processes in which these 2-component coating compositions are employed, and the coated articles produced by these processes.

Crosslinking polyisocyanates and binder components having isocyanate-reactive groups are generally known in the form, for example, of 2-component coating materials (cf. Kunststoff Handbuch, Volume 7, Polyurethane, 2nd Edition, 1983, Carl Hanser Verlag Munich Vienna, pp. 540-561). These 2-component coating compositions comprise as their binder, for example, a polymeric polyol and, as their crosslinker component (hardener), a compound having two or more free isocyanate groups.

The service properties of coating materials whose polymeric binders have been crosslinked with the isocyanates are much better than those of systems comprising low molecular mass binders. This relates in particular to service properties such as

- 20 - insensitivity to mechanical exposure such as tension, strain, impact or abrasion
- resistance to moisture (in the form of water vapor, for example) and to dilute chemicals
- 25 - resistance to environmental influences, such as temperature fluctuations and UV radiation
- 30 - high gloss of the coated surfaces.

The hardeners (curing agents) are expected not only to give the cured coatings the abovementioned service properties but also to improve, or at least have very little adverse effect on, the processing properties of the coating materials prior to their application.

So that the coating materials can be applied without problems by customary techniques - for example, by spraying them onto the surface to be coated - the coating materials are intended to possess a certain viscosity. Consequently, 2-component coating compositions normally comprise solvents. The high solvent content of these coating materials itself causes problems, however, since the coating-material processors are forced to take complex measures to avoid atmospheric emission of the solvents, which are released when the coating materials are applied and dried. The search has therefore been on for hardeners which do not greatly

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increase the viscosity of the binder-containing component or which, even better, reduce it. These hardeners themselves of course must not display any notable volatility at room temperature, as is the case with customary commercial monomeric isocyanates such as hexamethylene diisocyanate or isophorone diisocyanate.

In addition, following their application the 2-component coating compositions should cure as rapidly as possible so that the coated articles, following application, can be subjected rapidly to further processing or use.

Polyisocyanates comprising allophanate groups and biuret groups are known, for example, from EP-A-496 208, 524 501 and 566 037, where they are recommended for use as hardeners in 2-component coating systems. Structural components include aliphatic monoalcohols and all customary isocyanates. The structural components from the group of the cyclic monoalcohols, and hexamethylene diisocyanate and isophorone diisocyanate, are present in these documents only in the context of lists of the appropriate isocyanate and alcohol components. As evident from the experimental section of these documents, the focus is on polyisocyanates having allophanate and biuret groups which are derived from noncyclic alcohols.

The allophanates derived from these alcohols have the disadvantage, in particular, that the 2-component coating systems prepared therewith are relatively slow to cure and even following complete curing still have a level of surface hardness which is inadequate for many applications.

DE-A-42 29 183 discloses urethane- and isocyanurate-functional polyisocyanates of low viscosity. They are prepared by reacting, for example, cycloaliphatic alcohols, such as cyclohexanol, with an isocyanurate of hexamethylene diisocyanate to give the corresponding urethane.

Although the properties of the hardeners disclosed therein satisfy in most respects the customary requirements placed on the processing properties of the uncured liquid systems which comprise these hardeners and on the service properties of the coatings produced with the coating materials, the hardeners nevertheless still appear to be in need of improvement in terms of the viscosity of the coating systems, their curing rate, and the hardness of the coatings produced therewith.

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It is an object of the invention to provide this improvement.

We have found that this object is achieved by the compounds of the formula (I) defined at the outset, by mixtures and

- 5 2-component coating compositions which comprise these compounds and by articles which are coated with these 2-component coating compositions.

The diisocyanates of the formula (I) according to the invention  
10 are derived preferably from alcohols such as cyclohexanol, cyclohexanemethanol, cyclopentanol, cyclopentanemethanol, 3,3,5-trimethylcyclohexanol, menthol, norborneol, N-methyl-4-hydroxypiperidine, 4-(2-hydroxyethyl)morpholine or 4-(2-hydroxyethyl)pyrrolidone.

15

These diisocyanates can generally be prepared by reacting

- (i) isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) or a mixture of these isocyanates in the presence of  
20 a catalyst with a
- 5- or 6-membered cycloaliphatic alcohol in which up to 3 hydrogen atoms attached to one carbon atom may be substituted by C<sub>1</sub>-C<sub>4</sub>-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C<sub>1</sub>-C<sub>4</sub>-alkyl radical, or  
25
  - C<sub>1</sub>-C<sub>4</sub>-alkyl alcohol in which one hydrogen atom attached to a carbon atom is substituted by a 5- or 6-membered cycloalkyl radical in which up to 3 hydrogen atoms may be substituted by C<sub>1</sub>-C<sub>4</sub>-alkyl radicals and one or two methylene units may be substituted by an oxygen atom and/or a tertiary nitrogen atom which additionally carries a C<sub>1</sub>-C<sub>4</sub>-alkyl radical; a pyrrolidone radical or morpholine radical, where in the case of the two last-mentioned radicals, the nitrogen atom is attached to the alkyl radical of the alcohol;  
30
- 35
- 40 the molar ratio of said isocyanates to said monoalcohol being from 1.5:1 to 20:1,
- (ii) deactivating the catalyst and
- 45 (iii) removing any unreacted isocyanate.

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The molar mixing ratio of the HDI/IPDI mixtures is preferably from 0.1:1 to 10:1.

The reaction can be performed, for example, in the way described 5 in EP-A-524 501.

Examples of the catalysts used are quaternary ammonium salts, an example being N,N,N-trimethyl-N-(2-hydroxypropyl) ammonium 2-ethylhexanoate.

10

The reaction is generally conducted at temperatures from 50 to 150°C.

The reaction is ended by cooling the reaction mixture and 15 removing the catalyst, subjecting it to thermal decomposition or adding a suitable agent which deactivates the catalyst. Examples of suitable such agents are acids such as p-toluenesulfonic acids, dibutyl phosphate, or di(2-ethylhexyl) phosphate.

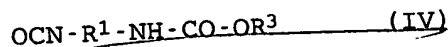
20 After the end of the reaction, unreacted hexamethylene diisocyanate or isophorone diisocyanate is generally removed by distillation, preferably down to a content of less than 0.5% by weight.

25 The reaction product, which is essentially free from isophorone diisocyanate or hexamethylene diisocyanate, has a viscosity of generally from 100 to 10,000, preferably from 150 to 6000 mPas, measured in accordance with ISO 3219.

30 ~~This method generally produces mixtures which may comprise, in addition to the diisocyanates (Ia), (Ib) and/or (Ic),~~

~~urethanes of the formula (IV)~~

35



in which the radicals R<sup>1</sup> and R<sup>3</sup> may have the following meanings: →

40

~~R<sup>1</sup>: a radical of the formula (II) or (III),~~

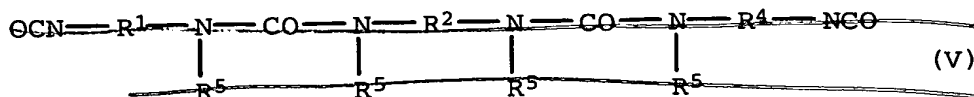
~~R<sup>3</sup>: the meaning indicated in claim 1; →~~

~~diisocyanates of the formula (V)~~

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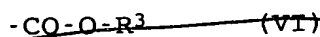
B  
3  
Inventor  
B.B  
3  
Inventor  
B.

B1  
case 10

5 in which the radicals  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$  and  $\text{R}^5$  may have the following meanings.

$\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$ : the meaning indicated for  $\text{R}^1$  in formula (I),

10  $\text{R}^5$ : 2 of the total of 4 radicals are hydrogen and the other two radicals are a radical of the formula (VI)



15 with the radicals  $\text{R}^5$  having the same meaning being separated by the unit  $\text{R}^2$ , and

20 - isocyanurates composed of 3 molecules selected from the group consisting of isophorone diisocyanate and hexamethylene diisocyanate.

Generally, in these mixtures

- 25 - the sum proportion of the diisocyanates (Ia), (Ib) and (Ic) is from 5 to 100% by weight,
- the proportion of the urethanes of the formula (IV) is from 0 to 20% by weight,
- 30 - the proportion of the diisocyanates of the formula (V) is from 0 to 30% by weight and
- the proportion of the isocyanurates each composed of 3 molecules selected from the group consisting of isophorone diisocyanate and hexamethylene diisocyanate is from 0 to 65% by weight.
- 35

40 Preferably, the weight ratio of diisocyanates (I) to monoisocyanurates (VII) is from 10:1 to 1:10.

Preferably, the sum of the proportions of the diisocyanates (Ia), (Ib), (Ic), (V), the urethane (IV) and the isocyanurate (VII) is from 10 to 100% by weight.

45

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If desired, the diisocyanates of the invention can easily be isolated from these mixtures by known separation methods such as gel permeation chromatography. Generally, however, this is unnecessary insofar as these diisocyanates (Ia), (Ib) and (Ic) are employed in the form of the abovementioned mixtures as crosslinkers in 2-component polyurethane coating compositions. The diisocyanates (Ia), (Ib) and (Ic) and the abovementioned mixtures comprising these diisocyanates are particularly suitable as component B in the preparation of 2-component coating compositions which as component A comprise a compound which carries polyisocyanate-reactive groups, preferably a hydroxy-functional polymer (A).

The hydroxy-functional polymers (A) are, for example, polymers having a hydroxyl group content of from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight. The number-average molecular weight  $M_n$  of the polymers is preferably from 1000 to 100,000, and with particular preference from 2000 to 10,000. The polymers concerned are preferably those which consist to the extent of more than 50% by weight of  $C_1$ - $C_{20}$ -alkyl (meth)acrylate, vinylaromatic compounds having up to 20 carbon atoms, vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinyl halides, nonaromatic hydrocarbons having 4 to 8 carbon atoms and 1 or 2 double bonds, unsaturated nitriles and mixtures thereof. Particular preference is given to those polymers which consist to the extent of more than 60% by weight of  $C_1$ - $C_{10}$ -alkyl (meth)acrylates, styrene or mixtures thereof.

The polymers (A) may additionally comprise hydroxy-functional monomers in accordance with the above hydroxyl group content and, if desired, further monomers, examples being ethylenically unsaturated acids, especially carboxylic acids, acid anhydrides or acid amides.

Examples of further polymers (A) are polyesterols, as are obtainable by condensing polycarboxylic acids, especially dicarboxylic acids, with polyols, especially diols.

Further suitable polymers (A) are polyetherols, which are prepared by addition reaction of ethylene oxide, propylene oxide or butylene oxide onto H-active components. Polycondensates of butanediol are likewise suitable.

The polymers (A) can of course also comprise compounds having primary or secondary amino groups.

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By way of example there may be mentioned products known as Jeffamines, i.e. amino-terminated polyetherols or oxazolidines.

In addition to the components A and B set out above, the  
5 2-component coating compositions may also comprise other polyisocyanates and compounds having polyisocyanate-reactive groups, as are normally present in 2-component coating compositions.

10 The molar ratio formed from the sum of the isocyanate groups in the components B to the sum of the isocyanate-reactive groups of component (A) is preferably from 0.6:1 to 1.4:1, particularly preferably from 0.7:1 to 1.3:1 and, with very particular preference, 1:1.

15 The coating compositions of the invention may additionally comprise organic solvents, examples being xylene, butyl acetate, methyl isobutyl ketone, methoxypropyl acetate, N-methyl-pyrrolidone. Solvents are used to establish the low viscosity  
20 which is desired for the processing of the coating composition, i.e. for its application to substrates.

The coating compositions may of course include further additives customary in coatings technology, examples being pigments,  
25 fillers, leveling assistants, etc.

They may also contain catalysts for urethane formation, such as dibutyltin dilaurate.

30 The 2-component polyurethane coating compositions can be prepared in a known manner. Normally, components A and B are mixed before the coating compositions are applied to a substrate. Mixing takes place normally from 0 to 8 h before application. The desired viscosity can be established with solvents.

35 The polyurethane coating compositions can be applied in a customary manner by spraying, pouring, rolling, brushing, knife-coating, etc., in a sheetlike manner to substrates.

40 The coating compositions are particularly suitable for workpieces with surfaces made from metal, plastic, wood, woodbase materials or glass.

The articles coated by these processes feature a surface which  
45 has very good mechanical properties - in particular, good hardness, flexibility and chemical resistance. With the coating

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compositions of the invention, these properties are achieved after only a particularly short curing time.

#### Experimental section

5

A. Preparing the urethane- and allophanate-functional polyisocyanates

10 A.1 Preparing the urethane- and allophanate-functional polyisocyanates from HDI and monoalcohols, and comparative examples

15 Hexamethylene diisocyanate (HDI) was charged to a reaction vessel, under a nitrogen blanket, and the amount of OH component indicated in Table 1 was added. The mixture was heated to 80°C, 200 ppm by weight (based on diisocyanate) of the catalyst, N,N,N-trimethyl-N-(2-hydroxypropyl)ammonium 2-ethylhexanoate, were added, reaction was allowed to take place at this temperature, and the reaction was stopped on reaching the NCO content specified in Table 1 by adding 20 250 ppm by weight (based on diisocyanate) of di(2-ethylhexyl)phosphate. The reaction mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar in order to remove monomeric HDI. The residual content of HDI monomer was then below 0.2% by 25 weight.

Data for the end products are given in Table 1.

30 A.2 Preparing a urethane- and allophanate-functional polyisocyanate from IPDI and cyclohexanol

35 6 mol of IPDI were charged to a reaction vessel, under a nitrogen blanket and 1.2 mol (20 mol%) of cyclohexanol were added. The mixture was heated to 70°C, 800 ppm by weight (based on diisocyanate) of the catalyst specified in A.1 were added, reaction was allowed to take place at this temperature and the reaction was stopped at an NCO content of the mixture of 27% by weight by adding 1000 ppm by weight (based on diisocyanate) of di(2-ethylhexyl)phosphate. The reaction 40 mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar in order to remove monomeric IPDI.

45 The solid end product had an NCO content of 15.4% and a softening point at 43°C.

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A.3 Preparing a urethane- and allophanate-functional polyisocyanate from an IPDI/HDI mixture and cyclohexanol.

5 A mixture of 4 mol of HDI and 1.5 mol of IPDI was charged to a reaction vessel, under a nitrogen blanket, and 1.1 mol (20 mol%) of cyclohexanol were added. The mixture was heated to 80°C, 650 ppm by weight (based on diisocyanate) of N,N,N-trimethyl-N-(2-hydroxypropyl)ammonium 2-ethylhexanoate were added, reaction was allowed to take place at this  
10 temperature, and the reaction was stopped at an NCO content of the mixture of 31% by weight by adding 800 ppm by weight (based on diisocyanate) of di(2-ethylhexyl) phosphate. The reaction mixture was subsequently distilled in a thin-film evaporator at an oil temperature of 165°C and under 2.5 mbar  
15 in order to remove monomeric IPDI.

The end product had an NCO content of 17.1% and a viscosity at 25°C of 4310 mPas.

20 B. Production and testing of clearcoats from the polyisocyanates of the invention

By way of example, the polyisocyanates of the invention were mixed with a hydroxy-functional acrylate resin (Lumitol®  
25 H 136, BASF) and with various polyisocyanate hardeners (comparison coating material 1: Basonat® HI 100, BASF, comparison coating material 12: allophanate based on HDI with 20 mol% ethylhexanol) in accordance with stoichiometric OH/NCO proportions, and if required was catalyzed with dibutyltin dilaurate (DBTL, Merck) in order to accelerate curing.  
30 Adjustment to an application viscosity of 20 s (DIN 53 211 cup 4 mm flow nozzle) was made with butyl acetate. The processing times (potlives) of the coating materials were adjusted by way of the amount of catalyst added in such a way  
35 that drying times of about 1 h were attained. Coatings with a wet film thickness of 200 µm were applied to glass plates using a film-drawing frame. The resulting clearcoats were cured under standard climatic conditions for 7 days. The solids contents were determined in accordance with  
40 DIN V 53 216 Part 1.

The coating materials prepared with the crosslinkers of the invention have improved solids contents and a lower  
45 proportion of volatile organic constituents (VOC) relative to a standard isocyanate (coating material No. 1 compar.). This means that in order to obtain coating materials having the same viscosity, less solvent is required in the case of the

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coating materials prepared with the isocyanates of the invention.

Relative to an allophanate synthesized from noncycloaliphatic alcohols, the coating materials of the invention have a much higher initial hardness and ultimate hardness (cf. Tab. 4, coating material No. 12 (comparative expt.) with the coating materials of the invention). When N-alkylhydroxypiperidine is used, moreover, it is unnecessary to add a catalyst to cure the coating compositions.

All coating materials, moreover, display good flexibility, good adhesion and good scratch resistance.

15 Table 1: Reaction products of HDI and monoalcohols

	Experiment No.	Monoalcohol	Amount based on isocyanate (mol %)	NCO content of the mixture (% by wt.)	NCO content after distillation (% by wt.)	Viscosity at 25°C (mPas)
20	1	Cyclohexanol	5	40.2	20.7	1220
	2	Cyclohexanol	10	36.9	19.5	1120
	3	Cyclohexanol	15	35.7	18.3	890
	4	Cyclohexanol	20	34.1	17.4	770
	5	Cyclopentanol	5	40.1	21.0	980
25	6	Cyclopentanol	10	38.2	19.8	660
	7	Cyclopentanol	15	36.8	18.3	610
	8	Cyclopentanol	20	34.6	17.1	650
	9	Cyclohexanemethanol	20	35.8	16.0	360
	10	Cyclopentanemethanol	20	35.0	18.6	560
30	11	3,3,5-Trimethylcyclohexane	10	36.2	18.3	1830
	12	3,3,5-Trimethylcyclohexane	20	32.2	15.9	1620
	13	Menthol	20	34.6	14.5	1330
	14	Norborneol	10	35.8	19.0	1810
	15	Norborneol	20	33.0	16.9	1320
35	16	N-Methyl-4-hydroxypiperidine	10	36.0	12.9	1320
	17	N-Methyl-4-hydroxypiperidine	20	29.0	10.0	3340
	18	4-(2-Hydroxyethyl)-morpholine	5	39.1	18.3	4550
40	19	4-(2-Hydroxyethyl)-morpholine	20	28.1	15.3	3580
	20	N-(2-Hydroxyethyl)-2-pyrrolidone	20	32.3	16.2	2020
	21 (comparative)	n-Butanol	20	33.5	18.3	273
45	22 (comparative)	2-Ethylhexanol	20	31.2	16.5	343

Table 2: Improved VOC values relative to the prior art

Coating composition							
Coating material	1 (compar.)	2	3	4	5	6	7
Polyisocyanate (Tab. 1)	HI 100	5	6	7	1	2	3
Alcohol	—	Cyclopentanol			Cyclohexanol		
Hydroxy acrylate	H 136	H 136	H 136	H 136	H 136	H 136	H 136
% DBTL s.o.s. <sup>1)</sup>	0.05	0.1	0.1	0.1	0.1	0.1	0.1
Coating hardness							
Pendulum attenuation, König [swings]							
after 5 h	20	16	17	17	25	20	20
7 d RT+15 h 60°C	143	139	142	144	141	140	141
Volatile organic constituents							
VOC g/l	512	498	485	485	505	496	486

Table 3: Improved VOC values relative to the prior art

Coating composition					
Coating material	1 (compar.)	8	9	10	
Polyisocyanate (Tab.1)	HI 100	11	14	16	
Alcohol	—	3,3,5-Tri-methylcyclo-hexane	Norbor-neol	N-Methyl-4-hydroxy-piperidine	
Hydroxy acrylate	H 136	H 136	H 136	H 136	
% DBTL s.o.s. <sup>1)</sup>	0.05	0.1	0.1	—	
Coating hardness					
Pendulum attenuation, König [swings]					
after 5 h	20	13	13	111	
7 d RT+15 h 60°C	143	144	140	130	
Volatile organic constituents					
VOC g/l	512	495	492	477	

<sup>1)</sup> solid on solid

Table 4: Improved drying times relative to low-viscosity products of the prior art (comparable VOC values)

5	Coating composition				
	Coating material	12 (compar.)	13	14	15
	Polyisocyanate (Tab.1)	22	4	19	17
	Alcohol	2-Ethyl-hexanol	Cyclo-hexanol	N-(2-Hydroxyethyl)-morpholine	N-Methyl-4-hydroxypiperidine
10	Hydroxy acrylate	H 136	H 136	H 136	H 136
	% DBTL s.o.s.	0.1	0.1	0.1	—
15	Coating hardness				
	Pendulum attenuation, König [swings]				
	after 5 h	10	18	25	112
	7 d RT+15 h 60°C	117	136	135	135
Volatile organic constituents					
	VOC [g/l]	477	476	494	475

- 20 Lumitol H 136: solids content = 70%, OHN = 135  
 Basonat HI 100: HDI polyisocyanate, viscosity about 3000 mPas, solids content = 100%, NCO = 22%

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